

Photochemical Attachment of Reactive Cross-Linked Polymer Films to Si/SiO₂ Surfaces and Subsequent Polymer Brush Growth

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Thin films consisting of a mixture of acrylate/methacrylate monomers were photochemically attached to modified silicon wafer surfaces. Reactive functionality was embedded into the photopolymer film by adding alkoxyamine monomers (inimers) that facilitate polymer brush growth in subsequent polymerization reactions. We present a careful examination of each of the steps, from substrate preparation to silane coupling agent coating, photopolymer attachment, and polymer brush growth. Several 3-methacryloyloxypropyl silanes were evaluated as silane coupling reagents. The surface roughness of wafers increased from 0.2 to 0.6 nm after treatment with silane. Curing of a thin photopolymer film did not increase the surface roughness. Interestingly, brushes of d₈ polystyrene grown from the photopolymer surface displayed half the roughness of the underlying polymer layer, displaying a smoothing effect. All photopolymer films attached to the wafers utilizing a silane layer had excellent adhesion. We studied the film surfaces by water contact angle measurements, atomic force microscopy, and IR and X-ray photoelectron spectroscopies.

Introduction

The development of processes that enable commercial application of nanotechnology can be considered one of the grand challenges of the 21st century. Commercially viable methods for reproducibly making functional structures with dimensions below 100 nm are required for future advances in microelectronics, biotechnology, and data storage.¹ The number of so-called “nanofabrication” processes that can be found in the literature are many, but few show real promise in future large-scale, commercial manufacturing processes.² A number of next-generation lithography candidates have been evaluated in recent years, including 157 nm photolithography, extreme ultraviolet (EUV), and nano-imprint lithography. Despite significant research expenditures, 157 nm lithography activities have ground to a halt, and there are serious doubts about the commercial viability of EUV. Imprint lithographic processes, however, continue to attract a great deal of interest, owing to simplicity, potential low cost, and ability to replicate features as small as 20 nm over large areas.³

Our research has focused on a novel imprint lithographic process called nanocontact molding for the replication of precisely defined, nanoscopic, functionalized polymeric features on surfaces.^{4–6} By using an imprinter consisting of a highly cross-linked polymeric mold supported on a transparent support we can accurately reproduce features ranging in size from macroscopic to 5 nm. An analysis of contact mechanics and advantages of utilizing this imprint process has recently appeared.⁷ The patterned resist layers used in most UV-assisted imprint processes are based on photocurable methacrylate/acrylate monomer compositions that are applied to the surface and cured while in contact with the transparent imprint template.^{4,7}

For some time various silane coupling agents have been used to modify the adhesion and release properties of oxide surfaces.^{8,9} Unfortunately, many of the protocols for silane coupling reagents in microelectronics applications are unreported or buried in the patent literature. Both adhesion and release play key roles in nano-imprint lithography. Because some UV-assisted imprint techniques, like step and flash imprint lithography, require the use of expensive quartz

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masters, a significant amount of effort in developing release coatings has been reported.^{2,3,10,11} There have been fewer reports on coatings used to promote adhesion of the UV-cured resist to the surface.^{5,6,12}

For the purpose of developing control of the chemistry and topology of nanopatterned surfaces, we have explored the covalent incorporation of functional comonomers (*inimers*) for controlled “living” free radical polymerization of polymer brushes from patterned polymer surfaces. Graft polymerization of polystyrene (PS) and polyacrylates from these embedded inimer sites was successfully performed and yielded polymer brushes which offer the ability to adjust chemical functionality and feature size in the nanometer size regime.⁵ This concept of taking advantage of embedded functionality in nanoimprinted features is a powerful and versatile technique to alter the surface properties of the patterned substrate.⁶

In UV-assisted imprint lithography where a patterned UV-cured photopolymer film is covalently bound to a Si/SiO₂ substrate, the interconnecting adhesion layer plays a crucial role. In cases where adhesion to the substrate is inadequate, serious delamination of patterned features can be observed. We show that the two groups in bifunctional molecules such as methoxy- or chlorosilanes bearing a 3-methacryloxypropyl group can be reacted with surfaces in an orthogonal fashion to provide an adhesion layer.¹³ Hence, 3-methacryloxypropylsilanes can be immobilized on a native SiO₂ layer in a condensation reaction with available Si—OH surface bonds, forming a thin layer and exposing a methacrylate group for further manipulation, for example, incorporation into a highly cross-linked polymeric network.

This paper presents an examination of the chemistry involved at the substrate/adhesion layer interface and at the adhesion layer/cross-linked polymer film interface. We place special attention on analysis of the surfaces, in terms of roughness and chemical modification. The importance of substrate preparation and the silane coating method is demonstrated, as small changes in procedure lead to significant changes in final film properties. We also present an example of polymer brush growth by nitroxide-mediated controlled “living” free radical polymerization (NM-LFRP) from these surfaces.¹⁴ Every step of surface manipulation was followed by atomic force microscopy (AFM) imaging along with water contact angle measurements and ellipsometry.

Experimental Section

Materials. Single-side polished 1 in. silicon wafers (diameter, 25.4 ± 0.3 mm; thickness, 254 ± 50 µm; phosphorus doped;

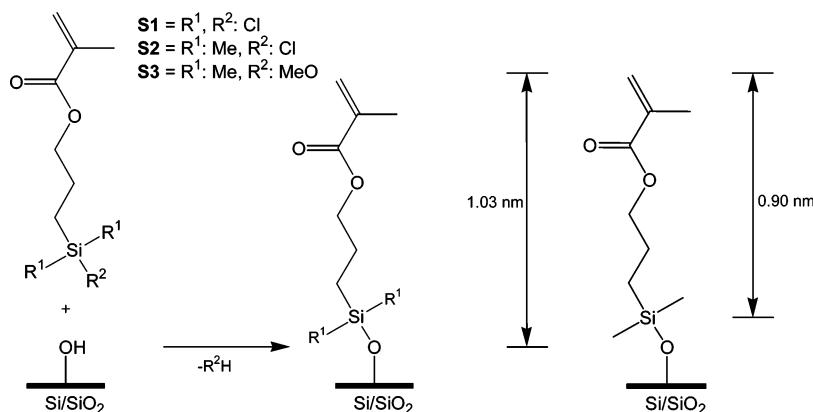
orientation, <100> off 1.5° toward <110> ± 0.5°; resistance, 8–12 Ω/cm) were obtained from Virginia Semiconductor, Inc. The silanes, 3-methacryloxypropyltrichlorosilane (**S1**), 3-methacryloxypropyltrimethylchlorosilane (**S2**), and 3-methacryloxypropyltrimethylmethoxysilane (**S3**; Gelest) were stored under Argon and used as received. Anhydrous toluene (99.9+ %, Aldrich), chlorobenzene, ethoxylated (2) bisphenol A dimethacrylate (Sartomer), 1-vinylpyrrolidin-2-one (Aldrich), acrylic acid 2,2-bis-acryloyloxyethylbutyl ester (Aldrich), and propylene glycol methyl ether acetate (PGMEA, Aldrich) were used as received. 2,2-Dimethoxy-1,2-diphenylethane (Aldrich) was recrystallized prior to use. The alkoxyamine inimer (NO), (2-methylacrylic acid 4-[1-[*N*-*tert*-butyl-*N*-(2,2-dimethyl-1-phenylpropyl)aminoxy]ethyl]benzyl ester) and nitroxide-mediated polymerization (NMP) initiator (*N*-*tert*-butyl-*N*-(2-methyl-1-phenylpropyl)-*O*-(1-phenylethyl)hydroxylamine) were prepared according to published procedures.^{5,15} Styrene-*d*₈ (Aldrich) was filtered through activated Al₂O₃ to remove the inhibitor prior to use.

Instrumentation. Ellipsometry was performed using a Gaertner variable angle manual ellipsometer; the light source was a He/Ne laser with $\lambda = 632.8$ nm. The angle of incidence (from the normal plane) was 70°. Measurements were performed for three to five different spots on each sample. Film thicknesses were calculated from ellipsometric parameters (Δ and Π). Calculations were performed for the transparent double layer model (silicon substrate/native silicon oxide/alkyl silane layer/(polymer/air) with the following parameters: air, $n_0 = 1$; photopolymer + NO, $n_1 = 1.50$; alkyl silane layer, $n_2 = 1.45$; SiO₂ layer, $n_3 = 1.462$; silicon substrate, $n_s = 3.858$, $k_s = 0.018$ (imaginary part of the refractive index). The thickness of the SiO₂ layer was fixed at 20 Å. Profilometry data were taken on a DEKTAK 3 Series surface profiler (Veeco Instruments). Water contact angle measurements were observed using a VCA 2500 video contact angle goniometer equipped with a Hamilton syringe having a flat-tipped needle. Deionized (DI) water was used as the probe fluid after filtering numerous times through a 20 nm syringe filter. The drop size was 1.00 µL. All reported values are the average of three to five measurements of drops on different areas of the sample surface. The modified surfaces exhibited homogeneous coating as evidenced by a tight distribution of measured contact angles; measured values were typically within ±1° of the average. IR measurements were recorded in both transmission mode and grazing angle total reflectance (GATR) on a Thermo-Nicolet Nexus 670 Fourier transform infrared (FT-IR) spectrometer with a GATR attachment. AFM images were collected on a Digital Instruments Dimension 3100 in intermittent contact mode under ambient conditions using silicon cantilevers (spring constant 0.58 N/m) and a scan rate of 2 µm/s. The root-mean-square (RMS) roughness was calculated with the AFM manufacturer’s provided software on images of 1 µm × 1 µm scan size. Stud pull adhesion testing was performed on a Romulus Universal Mechanical Strength Tester (Quad Group, Inc.). All stud pull tests were performed by bonding the pre-epoxy coated face of a nail shaped stud to the sample surface and then applying an exact perpendicular controlled rate of force until sample failure. The atomic concentrations of silicon, carbon, and oxygen were estimated by X-ray photoelectron spectroscopy (XPS). Analysis was done on an ESCA spectrometer with a monochromatic Al Kα X-ray source. Survey spectra at 1000 eV were recorded at 150 eV pass energy with a 1000 µm spot size for each sample. High-resolution spectra (50 eV pass energy, 20–30 eV window) were recorded for carbon, oxygen, and silicon. Variable angle XPS studies of the samples were conducted to estimate possible surface contamination.

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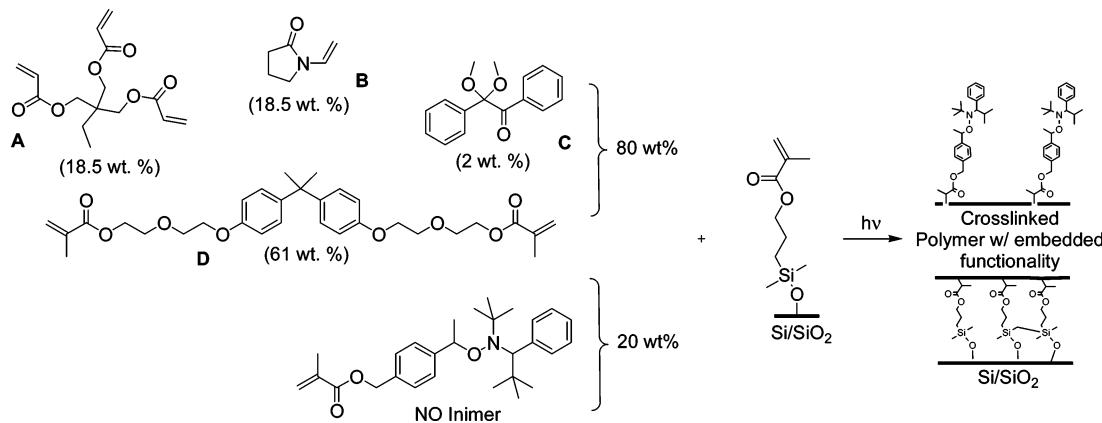
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Scheme 1. Idealized Representation of the Immobilization of Silanes S1, S2, and S3 on a Native SiO_2 Layer of a Si Substrate (Left) and Calculated Length of Surface Bound 3-Methacryloxypropyltrimethylsilane (Right)^a



^a MM2 energy minimization, Chem3D Pro 6.0 software package.

Scheme 2. Photoinitiated Cross-Linking by Radical Polymerization of an Acrylate/Methacrylate Resin To Yield a Highly Cross-Linked PMA/PMMA Film with Embedded Initiation Sites for Subsequent NM-LFRP, Covalently Bound to the Substrate Surface^a



^a XPS indicates that some of the NO inimer functionalities are located at the surface of the film.

Data were taken at two detector-to-sample angles: 15 and 75°. The 15° data provide information on approximately the top 15 Å of the film, while the 75° data sample the top 75 Å, assuming a mean free path of about 25 Å for the 1400 eV kinetic energy Si 2p photoelectrons through the polymer film. This estimate also assumes a flat sample surface.

Silicon Wafer Pretreatment. $\text{H}_2\text{SO}_4/\text{NoChromix}$. Silicon wafers were soaked in a concentrated sulfuric acid solution containing NoChromix for 5 min and rinsed extensively with DI water. The wafers were then rinsed in a DI water bath until the resistance of the water reached 7 Ω/cm. After 5 min in an 2-propanol vapor bath the wafers were dried in a clean oven.

UV/Ozone Cleaning. Cleaning of substrates via UV/ozone¹⁶ was accomplished using a SAMCO model UV-300H UV–ozone cleaner/stripper system.

Reaction of Silicon Wafers with 3-Methacryloxypropyl silanes. General Procedure (Scheme 1). In an argon atmosphere (glovebox), 1 in. wafers were placed in a vial and covered with anhydrous toluene (50 mL). A 1 wt % silane solution was prepared by adding the silane to the vial via a syringe. After 30–120 min the samples were removed, rinsed extensively with acetone and toluene, and then dried under vacuum at 70 °C for at least 1 h.

Preparation of Cross-Linked Polymeric Films with Embedded Inimer Functionalities (Scheme 2). The monomer solution

had the following composition: ethoxylated (2) bisphenol A dimethacrylate (61 wt %), 1-vinyl-pyrrolidin-2-one (18.5 wt %), acrylic acid 2,2-bis-acryloyloxymethyl-butyl ester (18.5 wt %), and 2,2-dimethoxy-1,2-diphenyl ethanone (2 wt %). The monomers and initiator were mixed and stored refrigerated in the dark prior to use. Immediately before use, the mixture was doped with 20 wt % of the inimer and diluted with PGMEA to yield 3–10 wt % solutions. This solution was filtered through a 0.2 μm syringe filter onto a cleaned and prepared (above) 1 in. silicon wafer and spun at 2000 rpm for 30 s. Immediately thereafter the wafer was placed in a transparent nitrogen-filled chamber and exposed using 365-nm light (14 mW/cm²) for 10 min to yield a highly cross-linked thin polymer film.

Alkoxyamine Initiated PS-*d*₈ Brush Graft Polymerization from Inimer-Embedded Network Thin Films. The silicon wafers coated with the photocured thin film network doped with 20 wt % alkoxyamine-based inimer were placed in a custom-made 5 mL Schlenk type glass vial. Styrene-*d*₈ (2.52 mL, 22.0 mmol), free alkoxyamine initiator (6.26 mg, 0.018 mmol), and chlorobenzene as a solvent (4.0 mL) were added. The solution was deoxygenated via three cycles of freeze, pump, thaw, and backfilling with N₂. The flask was sealed and heated at 125 °C for 7.5 h, after which time the wafers were removed and the solution was set aside for subsequent analysis. The wafers were rinsed liberally with THF and acetone, Soxhlet extracted with THF overnight, and dried in a vacuum oven at 70 °C for 2 h.

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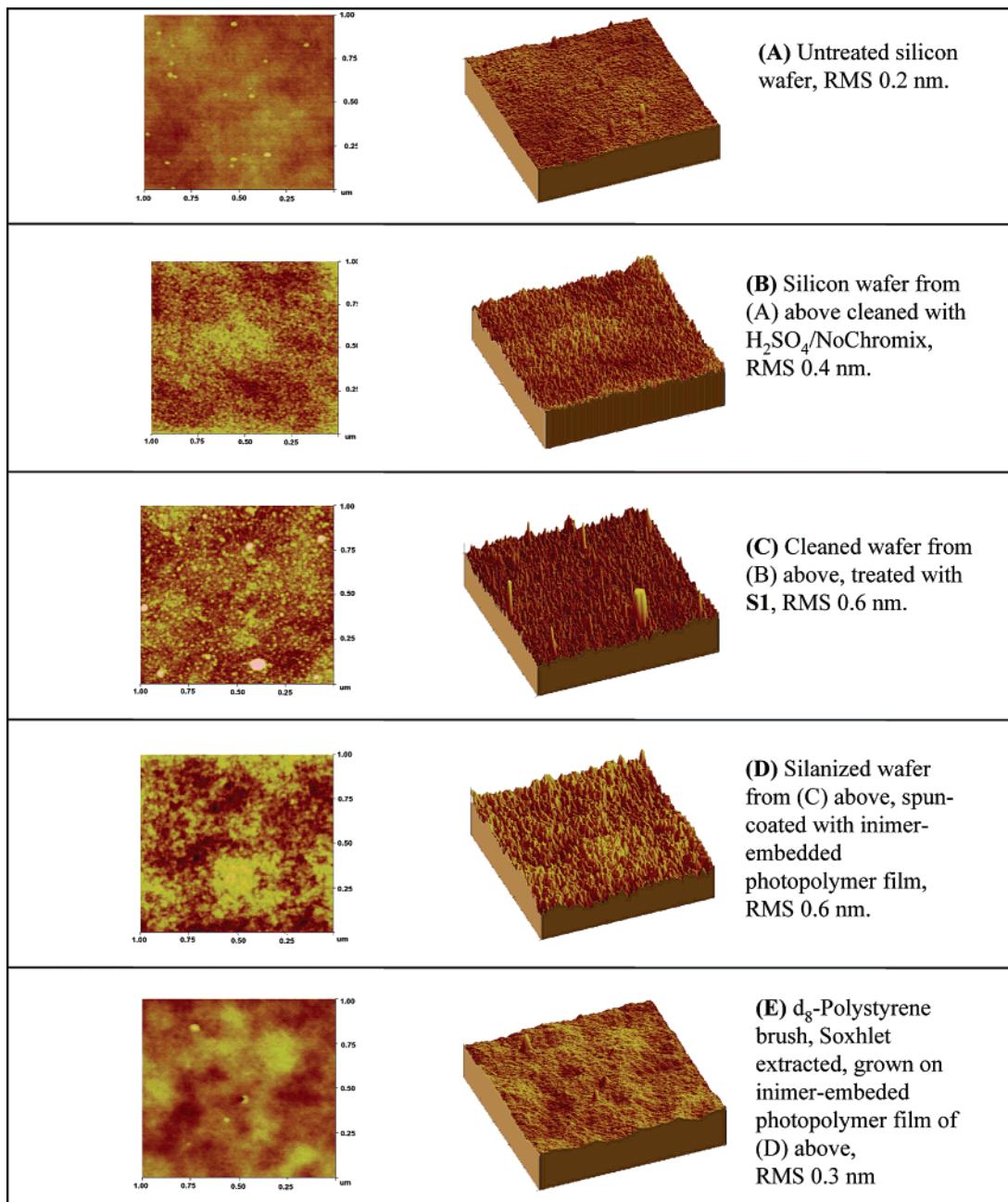


Figure 1. AFM images at five stages of functionalization, $1 \mu\text{m} \times 1 \mu\text{m}$, $z = 5 \text{ nm}$.

Results and Discussion

This study was driven by our desire to better understand and control the surface properties of treated silicon substrates and the subsequently attached thin photopolymer films. In the course of our study of nanocontact molding, we have noticed a wide variety of results, in terms of adhesion and film roughness, that seem to depend on substrate cleaning history and an adhesion promoter coating technique.

All of the surfaces were characterized by AFM to investigate the surface roughness of the various samples. First, we examined the silicon substrates. A typical AFM image of the surface of a Si wafer as it was received out of the carrier from the supplier (i.e., no additional cleaning) is shown in Figure 1A. The wafer surface appeared smooth with some randomly occurring artifacts, most likely dust and dirt particles. The RMS roughness as measured by AFM was

0.2 nm. Water contact angles varied quite a bit for wafers tested “as received” from the manufacturer. Large batch-to-batch variations were observed with measured values ranging from 20 to 50° which indicates that the wafer surfaces were easily contaminated by their environment during storage and shipment. Even within the same batch there are wafer-to-wafer differences. After oxidative cleaning in a $\text{H}_2\text{SO}_4/\text{NoChromix}$ bath the silicon wafer surface increased only slightly in roughness to 0.4 nm (Figure 1B). Alternatively, when an UV/O_3 etch¹⁶ cleaning procedure was used, the surface remained smooth with a roughness of 0.17 nm. Even though the solution cleaning procedure produced a slight increase in surface roughness we found it more convenient for batch processing of wafers and did not observe differences in subsequent reactivity of the wafer surfaces. The water contact angles of the wafers cleaned by both methods

ranged routinely between 14 and 18°. The measured water contact angle increased over time. Cleaned wafers that were allowed to sit in the lab in ambient atmosphere unprotected for days or weeks approached the original values observed for uncleared wafers. Care must be taken to use fresh cleaning solutions. Particle contamination and contact angle both increased with the age of the cleaning solution, with noticeable decrease in cleaning effectiveness after 1 day. We recommend always using a freshly prepared solution to obtain the most reproducible results.

The clean wafers were immersed in a toluene solution of 3-methacryloxypropylmethoxysilane, **S1**, at 25 °C for 8 h. After reaction, the wafers were extracted with clean toluene and dried. A water contact angle of ~70° on the coated wafers corresponded to the hydrophobic character of the alkylsiloxane organic overlayer. Prior investigations of self-assembled monolayers of alkylsilanes predicted that the acrylate used in this study should also form a densely packed layer.¹³ While the surface interaction of silanes with oxide surfaces is strongly dependent on the actual silane functionality (monochloro, dichloro, trichloro, monoalkoxy, etc.), the alkyl group type (short, long, or branched chains), and the reaction conditions, our surface analytical data are consistent with a densely packed monolayer or a multilayer of a mixture of covalently attached monomeric and polymeric species.^{17,18} Water contact angle measurements, ellipsometry, and XPS data support this conclusion. Previously published studies demonstrate that data obtained from characterization of surface silanol derivatization on the nanometer level can vary from substrate to substrate.^{19–21}

The AFM images of the **S1** coated surface (Figure 1C) revealed an increased roughness of 0.6 nm. The additional topography in this system could stem from the grafting of polycondensation products of the trichlorosilane moiety. Studies¹⁸ have shown that steric forces limit the reaction of **S1** with surface Si—OH groups to ~two of the three chloro positions. Other possible reactions include horizontal and vertical oligomerization or polymerization of the trichlorosilane at the silicon dioxide surface in the presence of adsorbed water, yielding surface grafted 3-methacryloxypropylsiloxanes. Larger surface features might result from the physisorption of solution polymerized material of the mentioned siloxane type.

Wafers treated with monofunctional silanes, **S2** and **S3**, were even smoother, with no increase in roughness observed for **S2** surfaces and only a 0.1 nm increase for **S3** coated surfaces. There were few defects observed on these surfaces, and the water contact angles were identical to those of the **S1** treated surfaces. The monofunctional silanes are expected to react principally orthogonally to the surface, favoring densely packed smooth monolayers (1 nm thick). Addition of bases such as triethylamine to the organosilane coating

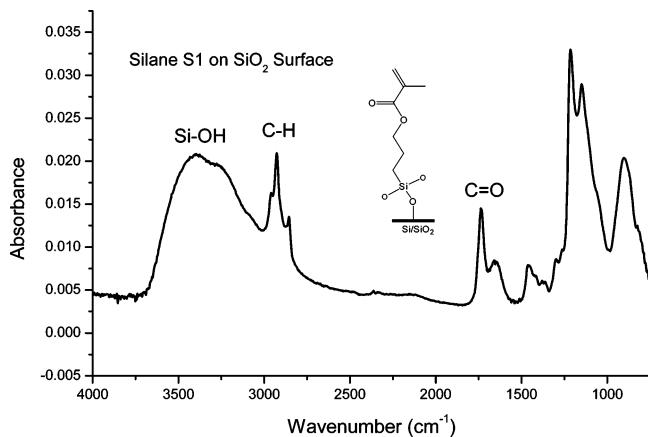


Figure 2. IR spectra of adhesion layer **S1**.

solutions resulted in large areas of contamination with a concurrent increase of roughness to >0.3 nm. Accordingly, we do not advise the use of amine bases, especially triethylamine, to facilitate the immobilization of silanes onto Si—OH surfaces unless a precise set of reaction conditions has been established by studying a sufficient number of reaction parameters and amines.¹⁸

The FT-IR spectrum of the 1 nm thick 3-methacryloxypropylsiloxane layer exhibits the expected vibrations (Figure 2). The aliphatic C—H signal at 2928 cm⁻¹ and the carbonyl stretch vibration at 1738 cm⁻¹ clearly indicate the presence of the silane. The broad signal at 3400 cm⁻¹ corresponds to free Si—OH groups in the 2 nm thick native SiO₂ layer.

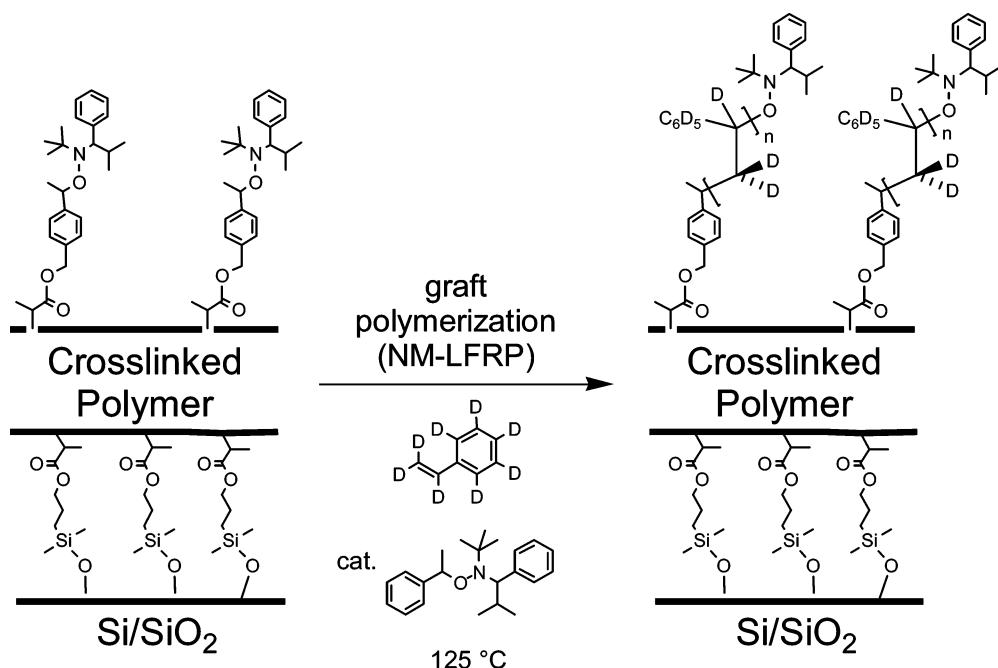
The next step of depositing the cross-linkable photopolymer film on the **S1**-silanized surface was accomplished by spin casting a PGMEA solution (3–10 wt %) of a photolytically polymerizable methacrylate/acrylate resin (Scheme 2). This mixture contained 20 wt % of an inimer compound consisting of two functional groups: a methacrylate moiety (monomer) that is involved in the photopolymerization and crosslinking reaction and an alkoxyamine unit (initiator) which acts as an initiation site for subsequent nitroxide-mediated “living” free radical polymerization.

The resulting thin liquid film containing monomers and photoinitiator was immediately exposed to a UV light source. The resulting photocured polymer film was covalently attached to the surface via the 3-methacryloxypropylsilane layer. The embedded inimer functionality was distributed throughout the polymer film; that is, some groups are advantageously presented at the surface and are available for subsequent brush growth from the polymer surface.⁵ Water contact angles of ~80–83° were higher than those of the adhesion layer (~70°) and those of photopolymer films that contain no inimer (~67°). This higher contact angle corresponds to the presence of inimer at the polymer surface and is supported by the XPS data presented below.

Film thicknesses ranged from 75 to 250 nm depending on the initial monomer solution concentration. The measured RMS roughness of the surface remained at 0.6 nm and was found to be independent of the film thickness (Figure 1D).

Though measurement of adhesive forces was not a goal of this study, some qualitative adhesion tests were performed. Photopolymerizable solutions do not wet cleaned, but otherwise untreated, wafers. Attempts to spin coat solutions

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Scheme 3. Surface Initiated NM-LFRP of Styrene-*d*₈ and the Formation of Polymer Brushes

onto untreated wafers resulted in massive dewetting and consequently inhomogeneous, poor quality films. Attempts were made to sandwich the photopolymer solution under an optically flat quartz wafer to create flat films, but after photopolymerization, films made in this fashion were of poor quality and delaminated from the substrates upon immersion in room temperature solvent baths such as toluene. In contrast, all of the silane-coated wafers, regardless of surface roughness, demonstrated wetting by the photopolymerizable solution and gave uniform, flat films by spin coating. The resulting photopolymerized films all demonstrated excellent adhesion to the silane-modified surface. In fact we could not remove the films by the classic Scotch tape test, nor would the films delaminate even after exposure to refluxing toluene. Attempts to test adhesion using a stud pull tester resulted in failure of the underlying silicon wafer. No polymer/substrate adhesive failure was observed when any of the silanes, **S1**, **S2**, or **S3**, were used to treat the wafers.

For the next step of growing polymer brushes from the inimer embedded surface, deuterated PS (PS-*d*₈) was selected.

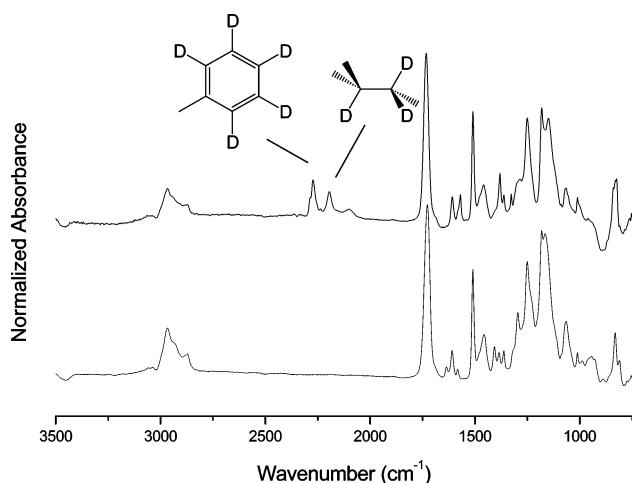


Figure 3. IR spectra of a spun cast inimer embedded photopolymer film, without (bottom) and with a PS-*d*₈ brush (top).

Previous studies have demonstrated the growth of PS brushes from similar surfaces, and the PS-*d*₈ surfaces will be used in future neutron reflectometry studies to address the question of the nature of the photopolymer/brush interface. In a typical brush polymerization, deuterated styrene was polymerized in chlorobenzene in the presence of a catalytic amount of a sacrificial NMP initiator at 125 °C for 7.5 h (Scheme 3).

The film thickness increase after brush growth was 33 nm, measured by ellipsometry. The uniform flatness and homogeneity of the samples indicates that we achieve good surface coverage of the polymer brush layer. To confirm the presence of covalently attached PS-*d*₈ brushes, FT-IR spectroscopy was used to characterize the composition of the polymer films before and after grafting (Figure 3). The FT-IR spectrum of the initial film collected in reflecting mode displayed peaks characteristic of a methacrylate network polymer, with the dominant peaks assigned to the carbonyl stretch (1726 cm⁻¹) and the C–H stretch (2966 cm⁻¹). After the network layer was subjected to surface polymerization conditions, new peaks were observed that correspond to a PS-*d*₈ brush. The aromatic and aliphatic vibrations of deuterated moieties clearly appear where expected at 2270 and 2194 cm⁻¹, a factor of 1.3–1.4 smaller than the frequencies of the corresponding vibrations involving hydrogen.²²

Grafting the deuterated PS brushes onto the photopolymer film caused the surface energy to drop as evidenced by the increase in the water contact angle to 89°. This value is in good agreement with reported contact angle measurements of 90–96° for pure PS films.²³ Surprisingly, the measured RMS roughness decreased to 0.3 nm (Figure 1E). This drop suggests that surface-initiated polymer brushes may be used to facilitate surface smoothing.^{21,23}

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Table 1. Analytical Data for the Sample Surfaces (as Illustrated in Figure 1)

sample ID	untreated	cleaned	S1 layer	inimer embedded photopolymer	<i>d</i> ₈ -PS brush layer
Water contact angle (°)	53.5	14.2	70.0	82.3	88.6
thickness ^a (nm)	—	2.2 ^b	1.1	237	270
RMS roughness ^c (nm)	0.2	0.4	0.6	0.6	0.3

^a Ellipsometry. ^b Native SiO₂ layer. ^c AFM over area of 1 μm².

Table 2. XPS Analysis of Thin Film Samples on Si Wafers: Atom Concentration Percent from High Resolution Data^a

sample ID	Θ	C=O ^b	C resid. ^c	C 1s	N 1s	O 1s	Si 2p	Si metal	Si oxide
S1 Layer	289	285		400	533		99 eV	102.5 eV	
	15°	6.1	42.7	48.8		23.8	27.4	9.2	18.2
	75°	4.4	22.1	26.5		24.0	49.4	38.0	11.4
Inimer embedded photopolymer	15°		79.6	1.2	19.2				
	75°		77.4	0.80	21.8				
<i>d</i> ₈ PS brush layer	15°		99.2	0.12	0.72				
	75°		99.2	0.09	0.75				

^a Θ, takeoff angle between sample and analyzer axis. ^b From C 1s peak fit. ^c Residual C = (C 1s total peak area) – (C=O peak fit area).

The analytical data from contact angle measurements, ellipsometry, and AFM are compiled in Table 1. Film surfaces were also characterized by XPS (Table 2). The organosilane layer exhibited results consistent with a thin carbonaceous layer. Data taken at 15° revealed higher ratios of carbon-to-silicon and silicon oxide-to-silicon metal than when measurements were made at 75°. This angle dependence supports a model for a confined layer of hydrocarbon on a layer of silicon oxide which in turn lies on bulk silicon. After coating with a thin film of inimer-embedded photopolymer, no signals from silicon were observed at the surface. At both angles the ratios of C/N/O are ~79:1:20. Slightly higher carbon and nitrogen values near the surface (15°) indicate a likely enrichment of inimer (alkoxyamine) near the thin film surface. The PS-*d*₈ brush layer provided ratios of C/N/O of >99:0.1:<1, consistent with a PS surface.

Conclusion

To prepare good quality thin films of photopolymerized materials on silicon wafer surfaces, an educated choice of proper cleaning techniques and silane coupling agents is warranted. This is especially critical when the photopolymer layer is patterned or subjected to subsequent high temperature solvent treatments. Through careful study of surface treatments, we were able to compare different substrate cleaning methods, silane coupling agent treatments, and their effect on subsequent polymer brush growth.

Immersion of silicon substrates in H₂SO₄/NoChromix solution or treatment with UV/ozone gave clean, smooth oxide surfaces with Si–OH groups for subsequent reaction

with various 3-methacryloxypropylsiloxanes. Excellent surface coverage of silanes is achieved by heating the cleaned substrates in 1% organosilane solutions in toluene. These silanes present 3-methacryloxypropyl functionality at the wafer surface which reacts in the photopolymerization of acrylate/methacrylate monomer films leading to high quality network photopolymer films. While it is not possible to prepare good quality photopolymer films without the organosilane layer, films prepared using the silane layer demonstrated excellent adhesion even when subjected to harsh solvent treatments.

When photopolymer films were prepared containing alkoxyamine imers, XPS and contact angle measurements indicated an enrichment of nitroxide groups at the polymer surface from which polymer brushes were grown. AFM images of the surface of a deuterated PS polymer brush layer showed it to be significantly smoother than the underlying layer to which it is attached. This use of polymer brushes to smooth surface roughness could have great utility in areas such as nanolithography where line edge roughness presents limits and challenges to making successively smaller features.

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